

Lattice-Boltzmann Model of Amphiphilic Systems

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Abstract. – A lattice-Boltzmann model for the study of the dynamics of oil-water-surfactant mixtures is constructed. The model, which is based on a Ginzburg-Landau theory of amphiphilic systems with a single, scalar order parameter, is then used to calculate the spectrum of undulation modes of an oil-water interface and the spontaneous emulsification of oil and water after a quench from two-phase coexistence into the lamellar phase. A comparison with some analytical results shows that the model provides an accurate description of the static and dynamic behavior of amphiphilic systems.

Introduction. – Self-assembling amphiphilic system are characterized by a large variety of phases [1, 2]. Many of these are structured on mesoscopic length scales. Examples include the swollen lamellar phase, the microemulsion phase in ternary amphiphilic mixtures, and the sponge phase in aqueous amphiphile solutions. In all of these cases, the amphiphile assembles into two-dimensional sheets which separate space into two networks of oil- and/or water-channels, both of which span the whole system.

The mesoscopic structure leads to dynamical behavior which differs qualitatively from that of simple fluid mixtures. In addition to the diffusive dynamics of all components, hydrodynamic flow plays an important role. Three classes of theoretical models which include hydrodynamic effects have been employed so far. The first are time-dependent Ginzburg-Landau models [3, 4, 5] which are coupled to a linearized Navier-Stokes equation (*i.e.* generalizations of model H of Hohenberg and Halperin [6] to amphiphilic systems). The second are membrane models, in which the hydrodynamics of the solvent is taken into account [7, 8]. Finally, a lattice-gas model [9, 10] — similar in spirit to vector lattice models employed to study equilibrium properties of microemulsions [1] — has been formulated and applied to study the dynamics of these systems.

An interesting alternative to these descriptions of the hydrodynamics of complex fluids is the Lattice-Boltzmann (LB) approach [11, 12, 13, 14]. It has recently been shown how LB methods can be generalized to study the dynamics of non-ideal fluids [15, 16] and fluid mixtures

[17, 16, 18] with a given free-energy functional. In this paper we show how this approach can be extended to study the dynamical behavior of amphiphilic systems.

Lattice-Boltzmann Approach. – The basic variables of a LB model for two-component fluid mixtures are the “microscopic” distribution functions $f_i(\mathbf{r})$ and $g_i(\mathbf{r})$, which are related to the density ρ , density difference $\Delta\rho$, and velocity \mathbf{u} by

$$\rho(\mathbf{r}) = \sum_i f_i(\mathbf{r}); \quad \Delta\rho(\mathbf{r}) = \sum_i g_i(\mathbf{r}); \quad \rho(\mathbf{r})\mathbf{u}(\mathbf{r}) = \sum_i f_i(\mathbf{r})\mathbf{e}_i, \quad (1)$$

where i denotes the possible velocity states, $\mathbf{e}_0 = 0$, and \mathbf{e}_i with $i \geq 1$ are the unit lattice vectors. The dynamics of the system is determined by the temporal evolution equations

$$f_i(\mathbf{r} + \mathbf{e}_i, t + 1) = f_i(\mathbf{r}, t) - \frac{1}{\tau_\rho} [f_i(\mathbf{r}, t) - f_i^{eq}(\mathbf{r}, t)] \quad (2)$$

$$g_i(\mathbf{r} + \mathbf{e}_i, t + 1) = g_i(\mathbf{r}, t) - \frac{1}{\tau_\Delta} [g_i(\mathbf{r}, t) - g_i^{eq}(\mathbf{r}, t)]. \quad (3)$$

It has been shown in ref. [17] that the time dependence of $\Delta\rho(\mathbf{r})$, $\rho(\mathbf{r})$, and the momentum density is described by Cahn-Hilliard and Navier-Stokes equations on sufficiently large length scales when the zeroth and first moments of f_i^{eq} and g_i^{eq} are required to fulfill eq. (1), and, in addition

$$\sum_i f_i^{eq} e_{i\alpha} e_{i\beta} = P_{\alpha\beta} + \rho u_\alpha u_\beta \quad (4)$$

$$\sum_i g_i^{eq} e_{i\alpha} e_{i\beta} = \Gamma \Delta\mu \delta_{\alpha\beta} + \Delta\rho u_\alpha u_\beta, \quad (5)$$

where $\Delta\mu = \delta\mathcal{F}[\rho, \Delta\rho]/\delta\Delta\rho$ is the chemical potential for the density difference $\Delta\rho$, Γ is the mobility, and $P_{\alpha\beta}$ the pressure tensor. We choose $\tau_\Delta = (1 + 1/\sqrt{3})/2$ to minimize terms which break Galilean invariance [17].

Amphiphilic Systems. – Many equilibrium properties of ternary amphiphilic systems can be accurately described using a Ginzburg-Landau model for a single, scalar order parameter $\phi(\mathbf{r})$, which we identified with the local *density* difference, $\Delta\rho(\mathbf{r})$, of oil and water. This model is defined by the free energy functional [19, 1]

$$\mathcal{F}_\phi[\phi] = \int d^d r \{ c(\nabla^2 \phi)^2 + g(\phi)(\nabla \phi)^2 + f(\phi) \}. \quad (6)$$

We assume that the full free-energy functional, which includes the density field, can be written as $\mathcal{F}[\rho, \phi] = \mathcal{F}_\phi[\phi] + \mathcal{F}_\rho[\rho]$, where $\mathcal{F}_\rho[\rho] = \int d^d r \{ b(\nabla \rho)^2 + \psi(\rho) \}$. A similar model, with $g(\phi) = g_0 = \text{const.}$ in eq. (6) and a different ansatz for the free energy density $f(\phi)$ (see below), has been employed in ref. [18] to study the spinodal decomposition to the lamellar phase.

The first task in the construction of the LB model is to determine the pressure tensor $P_{\alpha\beta}$, which is defined by the condition of hydrostatic equilibrium

$$\partial_\beta P_{\alpha\beta}(\mathbf{r}) = \rho(\mathbf{r})\partial_\alpha \mu(\mathbf{r}) + \Delta\rho(\mathbf{r})\partial_\alpha \Delta\mu(\mathbf{r}), \quad (7)$$

in a system with external potential $\mu(\mathbf{r})$ for the density $\rho(\mathbf{r})$. The pressure tensor is not unique, since eq. (7) is invariant under the substitution $P_{\alpha\beta} \rightarrow P_{\alpha\beta} + G_{\alpha\beta}$ with $\partial_\beta G_{\alpha\beta} = 0$. Indeed, a Chapman-Enskog expansion shows that only the divergence of the pressure tensor appears in

the Cahn-Hilliard and Navier-Stokes equations. Eq. (7) can be solved by expanding in powers of $\phi(\mathbf{r}) \equiv \Delta\rho(\mathbf{r})$ and its derivatives. After some algebra, we obtain

$$P_{\alpha\beta} = p_0\delta_{\alpha\beta} + \tilde{P}_{\alpha\beta} , \quad (8)$$

where

$$\begin{aligned} p_0 = & 2c\phi(\nabla^2\nabla^2\phi) - c(\nabla^2\phi)^2 - 2g(\phi)\phi\nabla^2\phi - g(\phi)(\nabla\phi)^2 - g'(\phi)\phi(\nabla\phi)^2 \\ & - 2b\rho\nabla^2\rho - b(\nabla\rho)^2 + \phi f'(\phi) - f(\phi) + \rho\psi'(\rho) - \psi(\rho) \end{aligned} \quad (9)$$

is the (isotropic) local thermodynamic pressure, and

$$\begin{aligned} \tilde{P}_{\alpha\beta} = & 2b(\partial_\alpha\rho)(\partial_\beta\rho) + 2g(\phi)(\partial_\alpha\phi)(\partial_\beta\phi) + c\Lambda(\nabla^2\phi)^2\delta_{\alpha\beta} - 2c(\partial_\alpha\partial_\gamma\phi)(\partial_\beta\partial_\gamma\phi) \\ & + c(\Lambda - 2)\{(\partial_\alpha\phi)(\partial_\beta\nabla^2\phi) + (\partial_\beta\phi)(\partial_\alpha\nabla^2\phi)\} + 2c(1 - \Lambda)(\partial_\alpha\partial_\beta\partial_\gamma\phi)(\partial_\gamma\phi) \\ & + c\Lambda\phi(\partial_\alpha\partial_\beta\nabla^2\phi) - c\Lambda\phi(\nabla^2\nabla^2\phi)\delta_{\alpha\beta} + c(4 - \Lambda)(\partial_\alpha\partial_\beta\phi)(\nabla^2\phi) , \end{aligned} \quad (10)$$

with an arbitrary real number Λ , which reflects the non-uniqueness of the pressure tensor. For $c = 0$ and $g(\phi) = g_0$ eq. (10) reduces to the well known expression for inhomogeneous liquids [20].

Since this result is rather lengthy, it is important to see that eqs. (1) and (4) can be solved explicitly for *any* pressure tensor. In the case of the two-dimensional triangular lattice, the equilibrium distribution f^{eq} is found to be

$$f_0^{eq} = \rho - Tr P_{\alpha\beta} - \rho \mathbf{u}^2 \quad (11)$$

$$f_i^{eq} = -\frac{1}{6}Tr P_{\alpha\beta} + \frac{\rho}{3}(\mathbf{e}_i \cdot \mathbf{u}) - \frac{\rho}{6}\mathbf{u}^2 + \frac{2}{3}\rho(\mathbf{e}_i \cdot \mathbf{u})^2 + \frac{2}{3}P_{\alpha\beta}e_{i\alpha}e_{i\beta} . \quad (12)$$

The distribution g^{eq} can be obtained from eqs. (11) and (12) for f^{eq} by replacing $P_{\alpha\beta}$ by $\Gamma(\delta\mathcal{F}[\rho, \Delta\rho]/\delta\Delta\rho)\delta_{\alpha\beta}$. It can be shown easily that this result agrees with the solutions of the special cases studied in refs. [15, 17, 16].

Equilibrium Properties. – To test the correctness of the approach described above, we have followed refs. [15, 17, 16] and first studied the equilibrium properties of our model. We have checked both the density profiles and the phase diagram for the Ginzburg-Landau model introduced in ref. [21], with $f(\phi) = \omega_0(\phi^2 - \phi_b^2)^2(\phi^2 + f_0)$ and $g(\phi) = g_0 + g_2\phi^2$, and for a simple ideal-gas free-energy density $\psi(\rho) = T\rho\ln(\rho)$. The deviation of the LB results from the solutions of the mean-field equations is on the order of a few percent if the parameters are chosen such that the interface width is at least several lattice constants. The phase diagram is determined by studying the stability of the microemulsion phase with respect to small density fluctuations. Similarly, the phase transition between the lamellar phase and oil-water coexistence is located by looking for either the growth of lamellae or a coarsening of the bicontinuous oil-water network after a quench from the microemulsion phase. In both cases, the transitions are found to agree within a few percent with those of the mean-field phase diagram.

Undulation Modes. – Due to the presence of the amphiphile, interfaces in amphiphilic systems can have an ultralow interfacial tension σ . The fluctuations of an interface are controlled in this limit by the bending rigidity κ . For the typical length scales of amphiphilic systems, the hydrodynamic flow is usually in the low-Reynolds-number, creeping-flow regime. In this case, a calculation of membrane fluctuations in the Stokes approximation [7] shows that the spectrum of the undulation modes of wavenumber k is given by

$$\omega(k) = \frac{i}{4\eta}(\sigma + \kappa k^2)k , \quad (13)$$

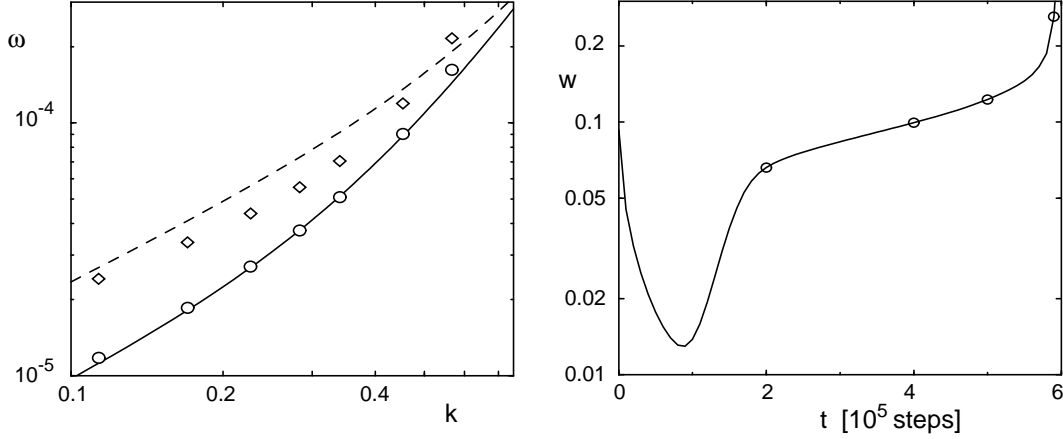


Fig. 1. – Spectrum of undulation modes. The parameters are $c = 0.01$, $\omega_b = 0.01$, $\phi_b = 0.5$, $f_0 = 0.1$, $g_2 = 4\phi_b(\sqrt{c\omega(1+4f_0)} - g_0) + 0.01$, $\Lambda = 0.123$, $b = 0.05$, $T = 0.5$, $\Gamma = 0.1$, and $\tau_\rho = 5.0$. Results are shown for $g_0 = +0.004$ (\diamond , dashed line) and $g_0 = -0.004$ (\circ , full line), which correspond to large and small σ , respectively.

Fig. 2. – Interface width w after a quench of a system from oil-water coexistence into the lamellar phase. The parameters are the same as in fig. 1, except for $\tau_\rho = 1.0$ and $g_0 = -0.0125$. The symbols indicate times for which the interfacial tension profile is shown in fig. 4.

where η is the shear viscosity. We have determined the relaxation times of the undulation modes of different wavelengths from our LB model of lattice sizes 64×128 and 128×128 with periodic boundary conditions. The results are shown in fig. 1 for two values of the parameter g_0 , which we use to tune the interfacial tension [21]. One of the big advantages of the LB approach used here is that *all* the coefficients in eq. (13) can be determined independently — σ and κ from a study of the elasticity of curved interfaces in the Ginzburg-Landau model [21, 1], and $\eta = (2\tau_\rho - 1)/8$ from a Chapman-Enskog expansion of the Boltzmann equation (2) [16]. The simulation results can therefore be compared directly with theory. It can be seen from fig. 1 for two values of the interfacial tension that the agreement is very good; the almost perfect agreement for $g_0 = -0.004$ is fortuitous, however.

We have checked explicitly that our results do *not* depend on the parameter Λ in the pressure tensor, eq. (10), as they should.

Spontaneous Emulsification. – When a system is taken abruptly from oil-water coexistence into the region of the phase diagram where the lamellar phase is stable, the large oil- and water-domains have to break up and form a intertwined structure on a much smaller length scale. To study this process in the LB scheme, we equilibrate a system of equal oil- and water-content in a *metastable* state of oil-water coexistence — with a planar interface — inside the lamellar regime. We then disturb the interface position by a sinusoidal capillary wave of the largest possible wavelength. The behavior of the interface is monitored by measuring its width $w = (1/L)\sqrt{\sum_i h^2(x_i)}$, where L is the number of lattice points, and x is the coordinate parallel to, and $h(x)$ is the local distance from, the initial planar interface. The time dependence of w is shown in fig. 2. The width first decreases due to a relaxation of the local interface profile, and a decrease in the amplitude of the capillary wave. After about 10^5 time steps, w increases again due to the increase of the amplitude of a mode of half the wavelength of the original perturbation. This mode is excited due to anharmonic terms in an effective

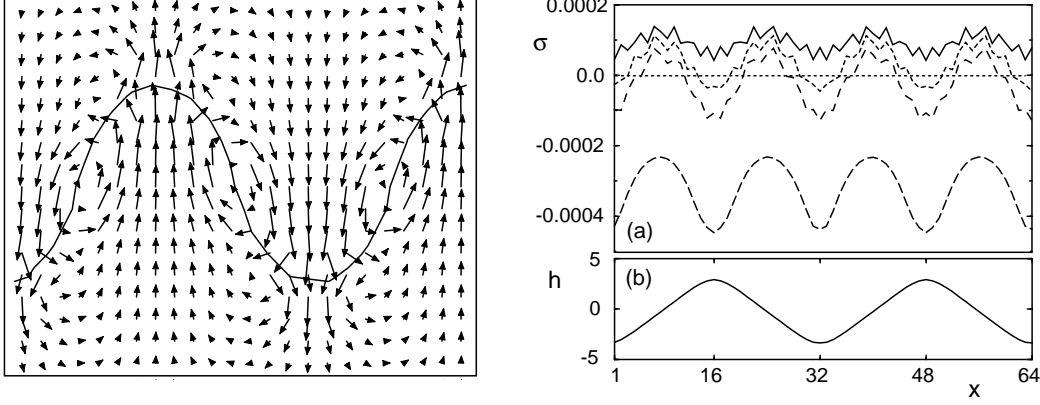


Fig. 3. – Typical flow pattern some time after the quench, where a large deformation of the interface has developed. Only a part of the full lattice and a subset of the velocity vectors is shown. The parameters are the same as in fig. 2.

Fig. 4. – (a) Variation of the local interfacial tension $\sigma(x)$ parallel to the interface at various times after the quench (from top to bottom), as indicated in fig. 2. (b) Interface position $h(x)$ at the last time shown in (a). The parameters are the same as in fig. 2.

interface Hamiltonian which lead to the coupling of different — in particular to neighboring — undulation modes. The new mode dominates because its characteristic frequency is larger than that of the original mode, compare eq. (13). This mode grows slowly until, after about $6 \cdot 10^5$ time steps, w becomes comparable to the interface width. A typical flow pattern at this time is shown in fig. 3. At later stages of emulsification, the interface shape becomes very complicated, and a characterization by the width w is no longer possible.

It is interesting to study the early stages of the emulsification process in more detail. To do so, we have calculated the *local* interfacial tension, which is given by

$$\sigma(x) = \int dz [P_N(\mathbf{r}) - P_T(\mathbf{r})] , \quad (14)$$

where $P_N = P_{zz}$ and $P_T = P_{xx}$ are the normal and tangential components of the pressure tensor, respectively. The result is shown in fig. 4 for different times after the quench. After the initial relaxation, the interfacial tension takes a value, which is *positive*, but nearly vanishes. After $2 \cdot 10^5$ time steps, a periodic structure appears, with a wavelength *half* of that of the undulation mode. The smallest tensions are found at the maxima of the function $h(x)$, *i.e.* where the interface motion is the strongest, while the largest tensions are located at the inflection points of $h(x)$. After about $4 \cdot 10^5$ time steps, $\sigma(x)$ becomes *negative* at its minima. The growth of the interface width now accelerates; this is accompanied by a further decrease of the interfacial tension.

Thus, we find that the surface tension along the interface becomes *inhomogeneous* in the early stages of the emulsification process. This indicates that most of the new interfacial area is created at the points where the interface moves fastest.

Summary and Conclusions. – We have shown in this paper how the LB scheme for

non-ideal fluid mixtures, which has been introduced in refs. [17, 16], can be extended to describe amphiphilic systems. We have tested both the equilibrium and dynamical properties of our model and have found excellent agreement of the results with complementary theoretical approaches. The model has then been used to study the spontaneous emulsification of oil and water after a quench into the lamellar phase.

Another conserved density, which we haven't taken into account in our present model, is the density of the amphiphile itself. Ginzburg-Landau models, which include this density, have already been investigated in thermal equilibrium [1, 4], so that the construction of a LB model for this case should be straightforward. The diffusion of the amphiphile to the interface should lead to new dynamical phenomena [22].

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